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STUDY PROGRAM TO IMPROVE FUEL CELL PERFORMANCE BY PULSING TECHNIQUES

BY

M. L. KRONENBERG

PREPARED FOR

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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UNION CARBIDE CORPORATION

THIRD QUARTERLY REPORT

STUDY PROGRAM TO IMPROVE FUEL CELL PERFORMANCE BY PULSING TECHNIQUES

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STUDY PROGRAM TO IMPROVE FUEL CELL PERFORMANCE BY PULSING TECHNIQUES

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ABSTRACT

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It has been observed that heavy discharge pulses show varying degrees of improvement on the performance level of different type fuel cell electrodes. The purpose of this investigation is to define these conditions, and to conduct studies to develop an understanding of this pulsing effect.

Earlier results 1, 2 indicated that pulsing is primarily a catalyst reactivation treatment and is most effective in improving the performance of electrodes that are catalyst limited from the start, or become catalyst limited during the life of the electrode. Studies on nonporous platinum metal electrodes show that these electrodes show rapid losses in catalytic activity with time in a H₂-saturated solution. However, the catalytic activity can be restored electrochemically by oxidative (anodic) pulses, or by chemical oxidation. Recent studies have determined how various factors such as pulse duration, environmental factors, and temperature variation influence the decay rate of catalytic activity.

SUMMARY

Pulsing experiments were conducted on Cyanamid NA-198-A electrodes using the 50-ampere pulsing unit described in an earlier report². Pulsing effects for these electrodes were small but generally beneficial, and were observed only after several days of operation.

The influence of experimental parameters on the decay rate of nonporous platinum anodes was investigated. The catalytic activity decay rate for Pt in gas-saturated solutions was found to depend on such factors as pulse time, coulometric versus open circuit operation, exposure to "poisons" and reducing agents. Activity-decay studies were also conducted on platinized platinum, silver, and rhodium electrodes as oxygen cathodes. The improvements resulting from the discharge pulsing of cathodes were significant but of shorter duration than for anodic pulsing.

Capacitance measurements using an a.c. bridge confirmed the decline in capacity with time after pulsing as was observed and reported when using the interruption technique.

A strong temperature dependence of the "pulsing effect" was demonstrated. The temperature dependence of activity decay following an activation pulse was also shown.

The practical application of the beneficial effects of pulsing to large plastic-bonded carbon electrodes that have been tested for several weeks or more was successfully demonstrated.

INTRODUCTION

In order to obtain long life and a high operating level from a fuel cell, the catalyst must maintain its effectiveness for extended periods of time. Since experimental evidence indicates that activity of some types of catalyst deteriorate with usage, the useful life and operating level of a fuel cell depends to a great extent on the rate of catalyst deterioration. For this reason, any technique or method of periodically restoring catalyst activity would be extremely useful in extending life and maintaining performance levels of fuel cells.

In the course of a recent survey on the effect of mechanical and electrical pulsing on the performance of fuel cell electrodes, it was observed that under certain conditions heavy discharge pulses significantly improved the sustained performance level of fuel cells. Preliminary results indicated that this "pulsing effect" was related to catalyst reactivation. Because of the great importance of catalyst reactivation in extending useful fuel cell life, it was decided to conduct a detailed investigation of this pulsing effect.

MEETINGS AND CONFERENCES

There were several visits by NASA personnel to the Union Carbide Research Laboratories to discuss various aspects of the program with Dr. M. L. Kronenberg and others. The dates of the visits and personnel involved were the following:

	Personnel			
Date	NASA	Union Carbide Corp.		
March 26, 1965	M. Unger W. Aldred	M. L. Kronenberg K. V. Kordesch		
May 18, 1965	M. Unger	M. L. Kronenberg		
May 21, 1965	M. Unger	M. L. Kronenberg		
May 24, 1965	M. Unger	M. L. Kronenberg		
May 27, 1965	M. Unger W. Aldred	M. L. KronenbergG. SprogisG. E. Evans		

Dr. M. L. Kronenberg attended the 127th Meeting of the Electrochemical Society and presented a paper entitled "A Study of the Effects of Heavy Discharge Pulsing on Fuel Cell Electrodes," by M. L. Kronenberg and K. V. Kordesch.

FACTUAL DATA

Task I - Definition of Effect.

A. Purpose and Scope.

The purpose of this Task is to obtain experimental information about conditions under which heavy discharge pulsing shows a maximum beneficial effect. This information is to be obtained on solid platinum electrodes: Union Carbide thin, composite electrodes; and porous nickel electrodes. In order to better understand the problems involved, preliminary pulsing information was also obtained on Union Carbide baked-carbon electrodes, American Cyanamid, and Justi-type electrodes.

With the exception of the pulsing of Cyanamid electrodes using the heavy-duty pulsing unit, the task requirements pertaining to these various types of electrodes have been completed and reported^{1,2}. Because the experimental results have shown that the pulsing effect is primarily a catalytic effect, independent of the substrate, additional experiments have been performed on less complex nonporous-metal substrates to obtain more detailed pulsing information.

B. Experimental Equipment and Procedures.

The instruments used for pulsing have already been described in earlier reports. 1-3 The cells used for obtaining pulsing information on porous and non-

porous electrodes have also been previously described in these reports. For special high purity runs with nonporous electrodes, a Teflon-glass cell was constructed. All cell components in contact with the electrolyte were Teflon of metal. A drawing of this cell is shown in Fig. 1.

C. Experimental Results.

1. <u>Discharge Pulsing of Cyanamid NA-198-A Electrodes (40 mg/cm² Pt)</u> with Heavy-Duty Pulsing Unit.

The data obtained for heavy-discharge pulsing of Cyanamid electrodes are summarized in Table I. In obtaining these data, the electrode reference potential, before and after pulse, was adjusted to the specified value, and the current before and after the pulse was compared at the same potential. The pulse duration was 5 seconds. The cells were pulsed 6 to 10 times per working day in the course of a 2-hour period to obtain the required data. As with nonporous Pt electrodes², pulsing the anodes to positive potentials with respect to a mercuric oxide reference electrode required that the circuit be opened before restoration of steady-state current to permit the electrode potential to recover to its normal operating level.

TABLE I
PULSING DATA FOR CYANAMID NA-198-A ELECTRODES

Cathode Cath								Ratio of Current After ÷ by the
1	Electrode						After	•
1	Anode	1	-0. 875	-0.694	180	1050	172	0. 96
Cathode 1		1	-0.875	-0.605	172	1250	172	1.00
Cathode		1	-0.875	-0.491	172	1600	172	1.00
Anode 2 -0.875 -0.463 180 1800 182 1.01 Cathode 2 0.0 -0.250 190 1800 182 1.01 Cathode 2 0.0 -0.077 192 850 192 1.00 2 0.0 -0.131 197 1050 200 1.01 2 0.0 -0.236 200 1400 200 1.01 2 0.0 -0.246 200 1800 200 1.00 Anode 6 -0.875 -0.595 160 1750 160 1.00 Anode 6 -0.875 +0.330 245 4500 267 1.09 Cathode 6 0.0 -0.217 170 1250 175 1.03 6 0.0 -0.460 160 2300 160 1.00 Cathode 6 0.0 -0.460 160 2300 160 1.00 Anode 14 -0.875 -0.580 255 1850 270 1.06 14 -0.875 -0.580 255 1850 270 1.06 14 -0.875 -0.130 287 3000 320 1.08 14 -0.875 -0.130 287 3000 320 1.08		1	-D. 875	-0.454	172	1800	172	1.00
Anode	Cathode	1	0. 0	-0.091	195	1050	195	1.00
Anode		1	0. 0	-0.178	190	1400	190	1.00
Cathode 2 0.0 -0.077 192 850 192 1.00 2 0.0 -0.131 197 1050 200 1.01 2 0.0 -0.236 200 1400 200 1.00 2 0.0 -0.246 200 1800 200 1.00 2 0.0 -0.246 200 1800 200 1.00 Anode 6 -0.875 -0.595 160 1750 160 1.00 6 -0.875 -0.160 200 3250 215 1.08 6 -0.875 +0.330 245 4500 267 1.09 Cathode 6 0.0 -0.217 170 1250 175 1.03 6 0.0 -0.460 160 2300 160 1.00 Anode 14 -0.875 -0.750 250 1125 240 0.96 14 -0.875 -0.580 255 1850 270 1.06 14 -0.875 -0.130 287 3000 320 1.08 14 -0.875 -0.130 287 3000 320 1.08 14 -0.875 -0.130 287 3000 320 1.08			0.0	-0.250	190	1800	195	1.02
Z -0. 875 -0. 463 182 1600 188 1. 03 Z -0. 875 -0. 436 180 1800 182 1. 01 Cathode Z 0. 0 -0. 077 192 850 192 1. 00 Z 0. 0 -0. 131 197 1050 200 1. 01 Z 0. 0 -0. 236 200 1400 200 1. 00 Z 0. 0 -0. 246 200 1800 200 1. 00 Anode 6 -0. 875 -0. 595 160 1750 160 1. 00 6 -0. 875 -0. 160 200 3250 215 1. 08 6 -0. 875 +0. 330 245 4500 267 1. 09 Cathode 6 0. 0 -0. 217 170 1250 175 1. 03 6 0. 0 -0. 460 160 2300 160 1. 00 6 0. 0 -0. 600 160 3000 165 1. 03 Anode	Anode	Z	-0.875	-0.626	180	1400	182	1. 01
Cathode 2 0.0 -0.077 192 850 192 1.00 2 0.0 -0.131 197 1050 200 1.01 2 0.0 -0.236 200 1400 200 1.00 2 0.0 -0.246 200 1800 200 1.00 Anode 6 -0.875 -0.595 160 1750 160 1.00 6 -0.875 -0.160 200 3250 215 1.08 6 -0.875 +0.330 245 4500 267 1.09 Cathode 6 0.0 -0.217 170 1250 175 1.03 6 0.0 -0.460 160 2300 160 1.00 6 0.0 -0.460 160 2300 160 1.00 Anode 14 -0.875 -0.580 255 1850 270 1.06 14 -0.875 -0.130 287 3000 320 1.08 14 -0.875 -0.130 287 3000 320 1.08 14 -0.875 -0.040 320 3500 340 1.03		Z	-0.875	-0.463	182	1600	188	1. 03
Z		2	-0.875	-0.436	180	1800	182	1. 01
Z	Cathode	Z ·	0. 0	-0.077	192	850	192	1.00
Z 0. 0 -0. 236 200 1400 200 1. 00 Z 0. 0 -0. 246 200 1800 200 1. 00 Anode 6 -0. 875 -0. 595 160 1750 160 1. 00 6 -0. 875 -0. 160 200 3250 215 1. 08 6 -0. 875 +0. 330 245 4500 267 1. 09 Cathode 6 0. 0 -0. 217 170 1250 175 1. 03 6 0. 0 -0. 460 160 2300 160 1. 00 6 0. 0 -0. 600 160 3000 165 1. 03 Anode 14 -0. 875 -0. 750 250 1125 240 0. 96 14 -0. 875 -0. 580 255 1850 270 1. 06 14 -0. 875 -0. 130 287 3000 320 1. 08 14 -0. 875 -0. 040 320 3500 340 1. 03		Z	0. 0	-0.131	197	1050	200	1.01
Anode 6 -0.875 -0.595 160 1750 160 1.00 6 -0.875 -0.160 200 3250 215 1.08 6 -0.875 +0.330 245 4500 267 1.09 Cathode 6 0.0 -0.217 170 1250 175 1.03 6 0.0 -0.460 160 2300 160 1.00 6 0.0 -0.600 160 3000 165 1.03 Anode 14 -0.875 -0.750 250 1125 240 0.96 14 -0.875 -0.580 255 1850 270 1.06 14 -0.875 -0.130 287 3000 320 1.08 14 -0.875 -0.040 320 3500 340 1.03		Z	0. 0	-0. 236	200	1400	200	1.00
6 -0.875 -0.160 200 3250 215 1.08 6 -0.875 +0.330 245 4500 267 1.09 Cathode 6 0.0 -0.217 170 1250 175 1.03 6 0.0 -0.460 160 2300 160 1.00 6 0.0 -0.600 160 3000 165 1.03 Anode 14 -0.875 -0.750 250 1125 240 0.96 14 -0.875 -0.580 255 1850 270 1.06 14 -0.875 -0.130 287 3000 320 1.08 14 -0.875 -0.040 320 3500 340 1.03		2	0.0	-0.246	200	1800	200	1.00
Cathode 6 -0.875 +0.330 245 4500 267 1.09 Cathode 6 0.0 -0.217 170 1250 175 1.03 6 0.0 -0.460 160 2300 160 1.00 6 0.0 -0.600 160 3000 165 1.03 Anode 14 -0.875 -0.750 250 1125 240 0.96 14 -0.875 -0.580 255 1850 270 1.06 14 -0.875 -0.130 287 3000 320 1.08 14 -0.875 -0.040 320 3500 340 1.03	Anode	6	-0.875	-0.595	160	1750	160	1.00
Cathode 6 0. 0 -0. 217 170 1250 175 1. 03 6 0. 0 -0. 460 160 2300 160 1. 00 6 0. 0 -0. 600 160 3000 165 1. 03 Anode 14 -0. 875 -0. 750 250 1125 240 0. 96 14 -0. 875 -0. 580 255 1850 270 1. 06 14 -0. 875 -0. 130 287 3000 320 1. 08 14 -0. 875 -0. 040 320 3500 340 1. 03		6	-0.875	-0.160	200	3250	215	1. 08
Anode 14 -0.875 -0.750 250 1125 240 0.96 14 -0.875 -0.130 287 3000 320 1.08 14 -0.875 -0.040 320 3500 320 1.08 14 -0.875 -0.040 320 3500 340 1.03		6	-0.875	+0.330	245	4500	267	1.09
Anode 14 -0.875 -0.750 250 1125 240 0.96 14 -0.875 -0.580 255 1850 270 1.06 14 -0.875 -0.130 287 3000 320 1.08 14 -0.875 -0.040 320 3500 340 1.03	Cathode	6	0. 0	-0.217	170	1250	175	1. 03
Anode 14 -0.875 -0.750 250 1125 240 0.96 14 -0.875 -0.580 255 1850 270 1.06 14 -0.875 -0.130 287 3000 320 1.08 14 -0.875 -0.040 320 3500 340 1.03		6	0. 0	-0.460	160	2300	160	1.00
14 -0.875 -0.580 255 1850 270 1.06 14 -0.875 -0.130 287 3000 320 1.08 14 -0.875 -0.040 320 3500 340 1.03		6	0. 0	-0.600	160	3000	165	1. 03
14 -0.875 -0.130 287 3000 320 1.08 14 -0.875 -0.040 320 3500 340 1.03	Anode	14	-0. 875	-0.750		1125		
14 -0.875 -0.040 320 3500 340 1.03		14	-0.875	-0.580	255	1850		
		14	-0.875	-0.130	287	3000	320	
14 -0.875 +0.320 345 4600 355 1.03		14	-0.875	-0.040	320	3500	340	
		14	-0.875	+0.320	345	4600	355	1. 03

Beneficial pulsing effects for these electrodes were quite small (i. e., 10% or less) and were observed only after several days of operation. This indicates that initial performance is not primarily catalyst-limited. Anodes appear to have derived some beneficial effects from pulsing since the performance level at a constant potential of -0.875 volt versus a HgO reference improved with time. The cathode performance decreased slightly with time, as normally expected with cell operation, with no special effects noted from pulsing in this case.

2. Environmental Influence on Activity Decay of Platinum Metals.

The results obtained in our previous reports indicated that a highly active catalytic surface of Pt for the electrochemical oxidation of hydrogen is characterized by a surface-oxidized state that has been partially reduced. It was also shown that the Pt catalytic activity deteriorates with time in a H₂ atmosphere, and that the activity could be restored by electrochemical or chemical oxidation. Most of the experimental work this Quarter was concerned with verifying these conclusions by comparing activity decay under various conditions, i. e., in O₂-saturated solutions or in the presence of impurities which are also known to produce a decrease in catalytic activity. Measurements were also made of the catalytic activity decrease of other metals as anodic and/or cathodic catalysts.

2.1 Effect of pulse time on activity decay of platinum. A series of experiments was conducted to determine whether the rate of decay in catalytic activity of Pt was related to the duration of the activation pulse. Accordingly, pulses which were 1.6 volts positive to a reversible H_2 electrode were applied by means of the Wenking potentiostat for 5 seconds, 30 seconds, 5 minutes, and 15 minutes. After application of the "activating" pulse, the change in activity versus time in a H_2 atmosphere was determined. The current at $\eta = 10$ mv was taken as a measure of the catalytic activity.

In Fig. 2 are shown activity-decay curves as a function of time for the pulse durations shown. Each curve represents an average of 3 decay curves for each pulse time. The time sequence of the runs were randomized to avoid cumulative pulsing effects. The observed small net difference between the short pulses (5 or 30 seconds) and the long pulses (5 or 15 minutes) are not

conclusive because of the relatively small differences observed. Thus the question of whether or not the observed pulsing effects could also be attributed to "impurity" adsorption is still open.

Data obtained on current vs. time for smooth Pt (20 cm²) <u>during</u> the pulse for pulses ranging from 0.65 volt to 1.6 volts are shown in Fig. 3. The 0.65 and 1.05 v curves are mainly H_2 dissolution currents, although some surface oxidation occurs at 1.05 v. ⁴ The fact that pulses $\geq +1$.05 v give lower currents than the +0.65 v pulse supports the view that maintaining the surface in a uniformly oxidized state reduces the catalytic activity. The currents during the +1.6 pulse includes O_2 evolution and surface oxidation current.

- 2.2 Comparison of activity decay rate in H_2 , O_2 , and Ar saturated solutions. Since platinum was found to decline in catalytic activity in H_2 -saturated KOH solutions, it was decided to determine whether the rate of decline could be slowed down in O_2 or Ar saturated solutions. Accordingly, electrodes were uniformly pulsed at +1.6 v for 15 minutes and then permitted to remain at open circuit in H_2 , O_2 , and Ar saturated solutions. At periodic intervals the electrodes from O_2 and Ar saturated solutions were returned to H_2 -saturated solutions so that activity determinations could be made. (Here the current at $\eta = 20$ mv was used as a measure of the catalytic activity.) As shown in Fig. 4, the rate of activity decay for the gas-saturated solutions was H_2 -Ar> O_2 . This supports the contention that decline of catalytic activity is associated with surface oxide reduction.
- 2.3 Coulometric vs. open circuit decay rate. It was of interest to determine whether there would be a difference in the catalytic activity decay rate between electrodes left on open circuit and electrodes at which a net anodic reaction was taking place. The decay rates for these two cases are shown in Fig. 5. It is seen that the decay rate was slower when current was flowing than when the electrode was left on open circuit. This is interpreted to mean that there are competitive reactions for the dissolved H₂. The dissolved H₂ is used to reduce the oxide, or is oxidized electrochemically. The electrochemical oxidation appears to make less H₂ available for the reduction of surface oxide, hence the lower activity decay rate.

2.4 Effect of poisons and reducing agents. In our previous Quarterly Report, 2 it was noted that the catalytic activity of Pt could be restored by chemical oxidation with hot chromic acid solution. A series of experiments was conducted to establish whether strong reducing agents and so-called "poisons" would have the opposite effect—that of destroying catalytic activity. It was also of interest to note whether catalytic activity destroyed by adsorption of "poisons" or reducing agents could be restored by anodic pulsing. Accordingly, the electrode was maintained at +1.60, 1.05, or 0.65 v for 15 minutes, and the activity measured; it was then placed in the treatment solution for 1 minute, copiously rinsed in distilled water and the activity measured again. The results obtained for 1.6 v pulse are given in Table II.

TABLE II

SUMMARY OF IMMERSION TREATMENTS FOR PLATINUM

(Electrode Area = 5 cm²)

Solution for 1 Minute Immersion	i (ma) before Immersion	i (ma) after Immersion	i (ma) After 1.6 v Pulse
10 ⁻⁴ M (NH ₄) ₂ S	2.12	0.61	1.80
l N HCl	2.21	1.70	2. 15
3% KBH4 in 1 N KOH	1.91	1.62	1.80
5% CrSO ₄ in 1 N H ₂ SO ₄ (Prepared by reducing Cr ₂ (SO ₄) ₃ with Zn powder)	1.88	0.62	1. 92
Distilled Water	2.02	2. 00	2.00

The most effective compounds for reducing catalytic activity were (NH₄)₂S and CrSO₄. The ammonium sulfide is a strong reducing agent and poison, and the CrSO₄ is a strong reducing agent. It is interesting to note that catalytic activity was restored by the +1.6 v pulse. The chloride ion (HCl) adsorbs on the surface but does not reduce the surface oxide, and has only a minor effect on lowering catalytic activity. The borohydride also did not affect catalytic activity. It evidently did not function as a reducing agent under the conditions used.

2.5 Effect of pulse cycling. An experiment was performed to determine whether pulse cycling, i.e., causing a potential to fluctuate between +1.2 v (oxidation) and -0.05 v (reduction, H₂ desorption), was more effective in producing active catalyst than maintaining the electrode at a constant potential of

- +1.2 v for an equivalent length of time. The electrode was then cycled in the sequences indicated in Fig. 6, where the results of the experiment are also summarized. The results indicate that there is no advantage to cycling. Maintaining the electrode at a constant potential of +1.2 v produces the most active catalyst.
- 2.6 Decay of Rh and Pd in H_2 -saturated solutions. The activity decay of Rh in H_2 -saturated solutions was very similar to that reported for Pt. A summary of the data obtained thus far for activity vs. time studies in H_2 -saturated solutions on smooth Rh are given for 15-minute pulses to +1.6, 1.05, and 0.65 volt in Fig. 7. Activity decay for Pd was significantly different than Rh and Pt, and further verification must be done before the results can be reported.
- 2.7 Activity decay rates for O₂ cathodes. Polarization curves were determined on Pt-Pt, Ag and Rh electrodes as O₂ cathodes to establish a comparison polarization for the activity decay studies. The curves obtained for 20 cm² nonporous electrodes are given in Fig. 8. The activity of the metals as O₂ cathodes is Pt-Pt>Ag>Pt>> Rh. Based on these polarization curves, it was decided to run activity decay experiments at cathode-reference potentials of -10, -30, and -50 mv for Pt-Pt, Ag and Rh, respectively. The cathodes were pulsed to -300, -700, and -1000 mv electrode-reference potential regions for 15 minutes and activity vs. time studies were made. No clear-cut differences were noted between pulsing to these three potential regions. In all instances, significant improvement of a very short duration was noted. Results for the three metals pulsed to -700 mv vs. an HgO reference are shown in Fig. 9. In general, the improvements resulting from discharge pulsing of cathodes were of much shorter duration than for discharge pulsing of anodes.
- 2.8 Change of electrode capacity with time after pulsing in H₂-saturated solutions. Capacitance measurements by means of an a. c. bridge confirmed the decline in capacity with time after pulsing, as was observed when using the interruption technique. Both a Wayne-Kerr Q221 and a General Radio Model 1608 bridge were used. With this latter instrument it was necessary to use a low surface area electrode and a Pt wire (area = 0.77 cm²). In Table III are the results for capacity vs. time measurements for this electrode following a 15 minute pulse at +1.2 volts vs. a H₂-reference electrode in the same H₂-saturated 1 N KOH solution.

TABLE III
CAPACITY VS. TIME MEASUREMENTS

Time Since Pulse (hours)	Capacity μ F		
0. 000	139. 0		
0. 083	122. 0		
0.150	108.0		
0.630	100.0		
1.000	85. 0		
1. 750	83. 3		
2. 550	80. 0		
4. 530	72. 5		
5.410	53. 2		
22. 000	50.0		
22. 900	50. 0		

Task III - Temperature Effects.

The results of a series of experiments on the temperature dependence of pulsing effects were reported in the March Progress Letter. The results, based on the average improvement resulting from a single pulse (50 pulse comparisons were made—approximately 17 at each temperature), yielded the following data: $26\,^{\circ}$ C, $i_a/i_b = 1.18$; $45\,^{\circ}$ C, $i_a/i_b = 1.32$; $i_a/i_b = 1.35$; where i_a/i_b is the ratio of current-after-the-pulse to current-before-the-pulse obtained at a comparison polarization of 10 mv.

The entire experiment was repeated in more detail at four temperatures: 26°, 45°, 70°, and 90°C. The procedure used was the following:

- 1) The current at $\eta = 10$ mv was noted immediately before the pulse (i_b).
- 2) A 30-second pulse to +1.6 v was applied by means of the Wenking potentiostat. The current at η = 10 mv immediately after the pulse (i_a) was noted. the ratio i_a/i_b was taken as a measure of the improvement in catalytic activity resulting from the pulse.
- 3) The cell was allowed to remain at open circuit for 30 minutes, and the current was again noted (i_c) . The ratio i_c/i_a was taken as a measure of decay rate of catalytic activity.

In Fig. 10 are shown the results of i_a/i_b for the four temperatures. The mean values \pm their standard deviations are plotted, and the number of experimental points are shown below at each temperature. The mean value follows

the exponential curve, which is shown as a dotted line. Applying the statistical "t" test to the data yielded the "t" values shown in Table IV. The temperature dependence data supports the conclusion that there is a significant temperature effect for pulsing. However, the difference between this temperature effect ranging from 26 to 45°C is evidently quite small, and it was not possible to statistically verify the validity of this small difference for this one comparison.

TABLE IV
STATISTICAL VALUES SHOWING TEMPERATURE DEPENDENCE
OF IMPROVEMENT OF CATALYTIC ACTIVITY
RESULTING FROM A SINGLE PULSE

Temperature Comparison	''t'' Value	Confidence Level for Real Difference between the Two Temperatures
26 and 45°C	0.62	< 50%
26 and 70°C	3.30	> 99%
26 and 90°C	8.50	> 99%
45 and 70°C	2.50	99%
45 and 90°C	7.50	> 99%
70 and 90°C	3. 02	> 99%

The decay rate after 30 minutes (i_c/i_a) was also determined as a function of temperature, and these values are shown with the average points \pm the standard deviation in Fig. 11. Applying the statistical "t" test to this data yielded the results shown in Table V.

TABLE V
STATISTICAL VALUES SHOWING TEMPERATURE DEPENDENCE
OF DECAY-CATALYTIC ACTIVITY
30 MINUTES AFTER ACTIVATION PULSE

Temperature Comparison	''t'' Value	Confidence Level for Real Difference between the Two Temperatures	
26 and 45°C	0.41	< 50%	
26 and 70°C	2.04	95%	
26 and 90°C	4.45	> 99%	
45 and 70°C	1.44	83%	
45 and 90°C	3.62	> 99%	
70 and 90°C	2.63	> 99%	

The temperature dependence is real but quite small in the range of 26° to 45°C. The temperature dependence data presented in Figs. 10 and 11 are consistent with the "surface oxidation" theory discussed in our previous report. The rate of surface oxide formation would be expected to increase with temperature. This would be reflected in higher catalytic activity with increasing temperature obtained as a result of a single pulse, as was shown in Fig. 10. Once formed and left exposed to a reducing environment, the rate of oxide reduction would be greater at higher temperatures. This is reflected in the decreased activity 30 minutes following a pulse, as shown in Fig. 11.

Task IV - Life Testing.

A. Effect of Pulsing on "Run-Down" Electrodes.

A practical application of the "pulsing effect" was attempted on Union Carbide plastic-bonded carbon electrodes which were on continuous test in our laboratory. Cells were selected which showed far below normal performance for their age and test condition so as to provide a critical measure of pulsing effectiveness. Since these were sealed cells and no prior provision had been made for the insertion of a reference electrode, it was not possible to monitor the potential to which each electrode was driven. An arbitrary pulse of about ten times the steady-state current was applied to each cell. The results obtained on several cells are shown in Table I. These results are typical of many tested, ranging from minute improvements to improvements of up to 0.2 volt as a result of a single pulse. The duration of the improvements ranged from a few hours to weeks.

TABLE VI
EFFECT OF HEAVY DISCHARGE PULSES ON CELL PERFORMANCE

Steady	Steady State Current 8 Amps = 50 ma/cm ² ; Pulse Current = 50 Amps (315 ma/cm ²)							
C -11		Test	Cell Po		Improvement	Pulse		
Cell No.	Type	Time (hrs.)	(Volt Before Pulse	After Pulse	from Pulse (Volts)	Duration (seconds)		
		'						
656	$H_2 - O_2$	1776	0.81	0. 86	0. 05	2		
657A	H_2 -Air	3908	0.75	0.78	0.03	1		
657A	H_2 -Air	4312	0.65	0.74	0. 09	1.		
662	$H_2 - O_2$	780	0.82	0.88	0. 06	2		
665	$H_2 - O_2$	3400	0.68	0.80	0. 12	2		
665	$H_2 - O_2$	4000	0.68	0.76	0.08	2		
688	H_2 -Air	748	0.65	0. 85	0.20	2		

B. Effect of Pulsing on Justi-Type Electrodes (Obtained from Varta, A. G., Frankfurt, West Germany).

The effect of twice daily pulsing on the performance of Justi-type anodes and cathodes is summarized in Fig. 12. Anode half-cells were run continuously at 50 ma/cm², and the test cell was pulsed twice daily at a current density of 500 ma/cm² for five seconds. Cathode half-cells were run at 100 ma/cm² continuously, and the test cell was pulsed at 1000 ma/cm² for five seconds. An improvement in anode and cathode performance is suggested by the data. However, the standard deviation in the performance of these electrodes is not known so that the statistical confidence level of the results cannot be determined.

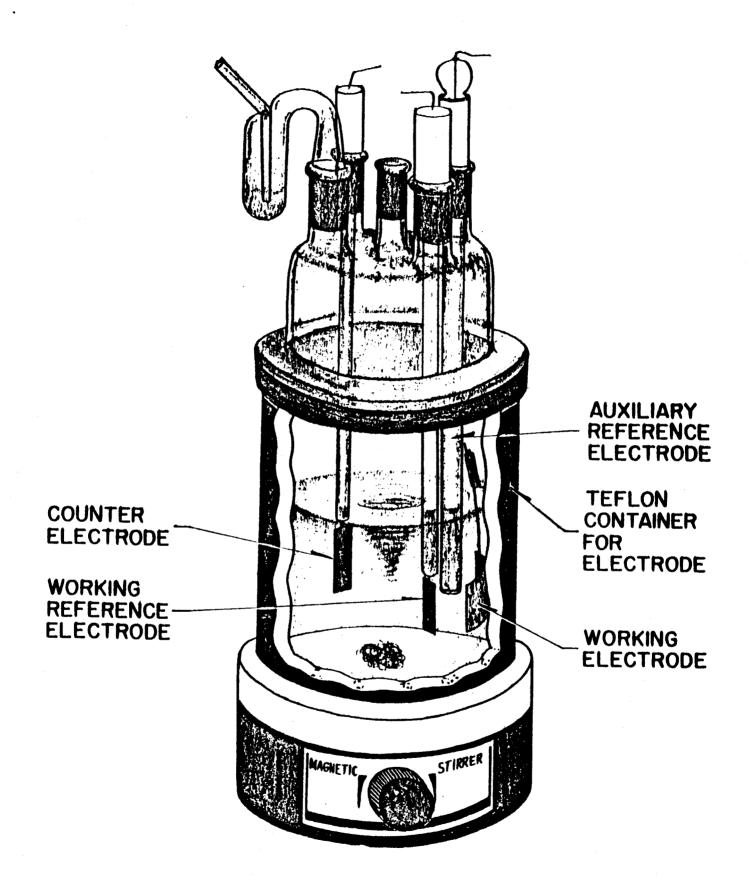
Future Work.

- 1. At the request of M. R. Unger, Technical Manager of this Contract for NASA, an experiment will be conducted to determine whether there are any discontinuities or singular points of response when a Cyanamid H₂-O₂ fuel cell is pulsed at 10 cycles/second increments up to 500 cycles/second.
- 2. Controlled potential pulsing experiments will be carried out on porous electrodes using a potentiostat with high current capabilities.
 - 3. The activity decay of solid Pd catalysts will be concluded.
- 4. Tests will be conducted in an applied system with Union Carbide composite electrodes to determine the optimum frequency of pulse application and open circuit time following a pulse.

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- 2. M. L. Kronenberg, "Ibid," NASA Report CR-54337 (Feb. 1965).
- 3. M. L. Kronenberg and K. V. Kordesch, "Ibid," NASA Report CR-54150 (June 1964).
- 4. A. Bethune in "The Encyclopedia of Electrochemistry," (C. Hampel, ed.), p. 426, Reinhold Publishing Corp., New York (1964).

APPENDIX



D-1984

Fig. 1 Teflon-Glass Cell Used for Polarization Measurements on Nonporous Electrodes.

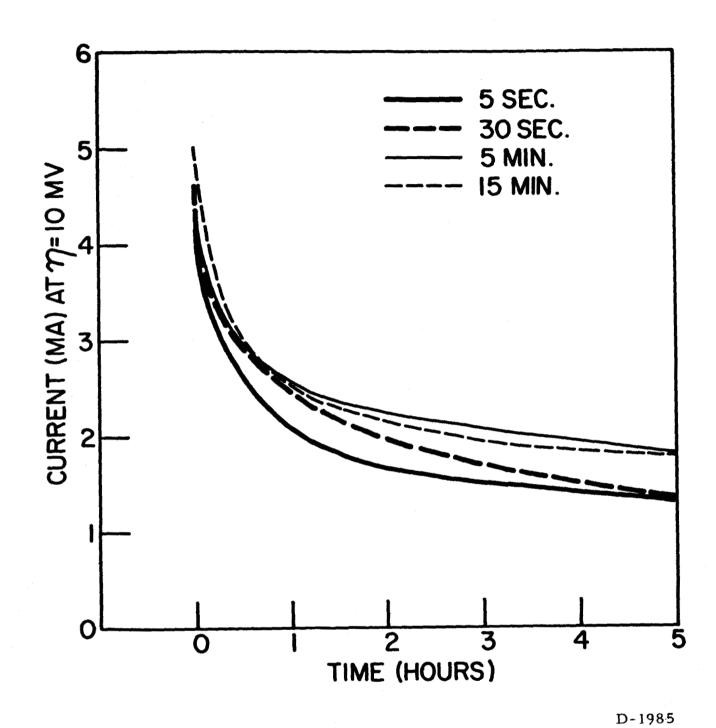


Fig. 2 Dependence of Decay in Catalytic Activity of Pt on Pulse Duration.

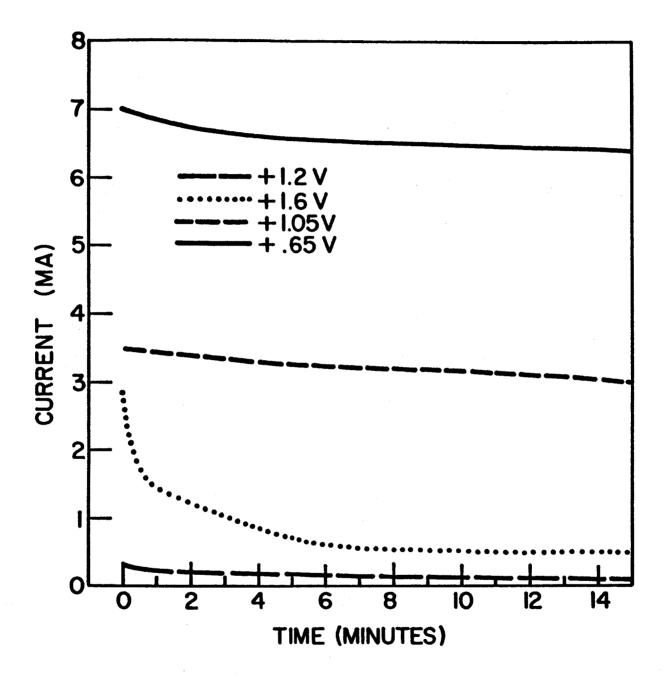


Fig. 3 Current Versus Time at Various Pulse Potentials.

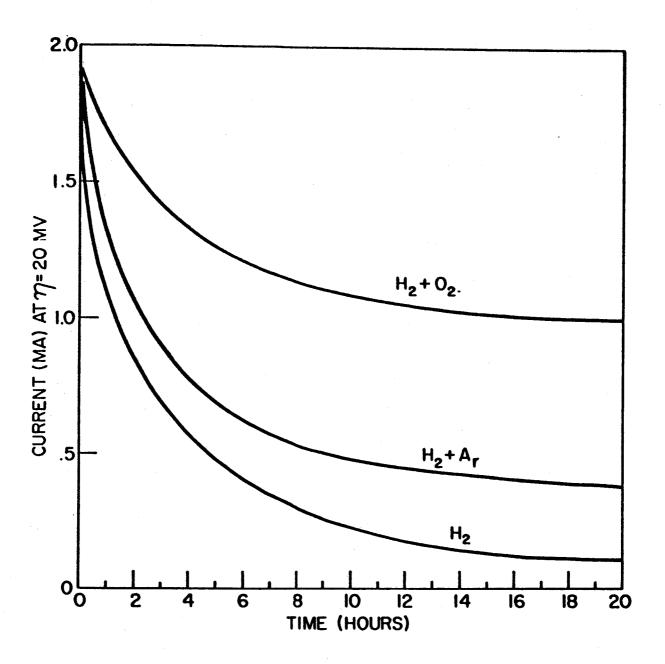


Fig. 4 Dependence of Activity Decay on Saturation Gas; Electrode, Pt-Pt; Area = 3 cm².

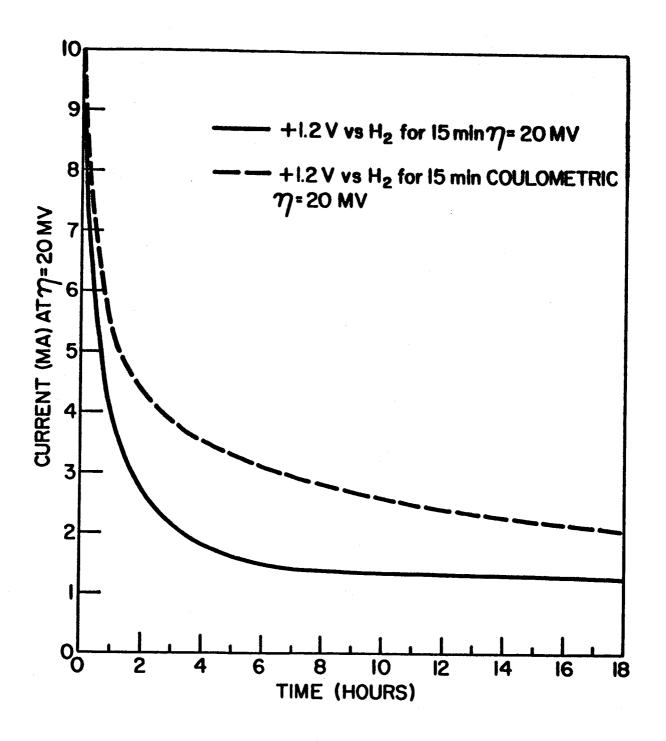


Fig. 5 Coulometric Versus Open Circuit Decay Rate of Pt in H₂-Saturated Solutions.

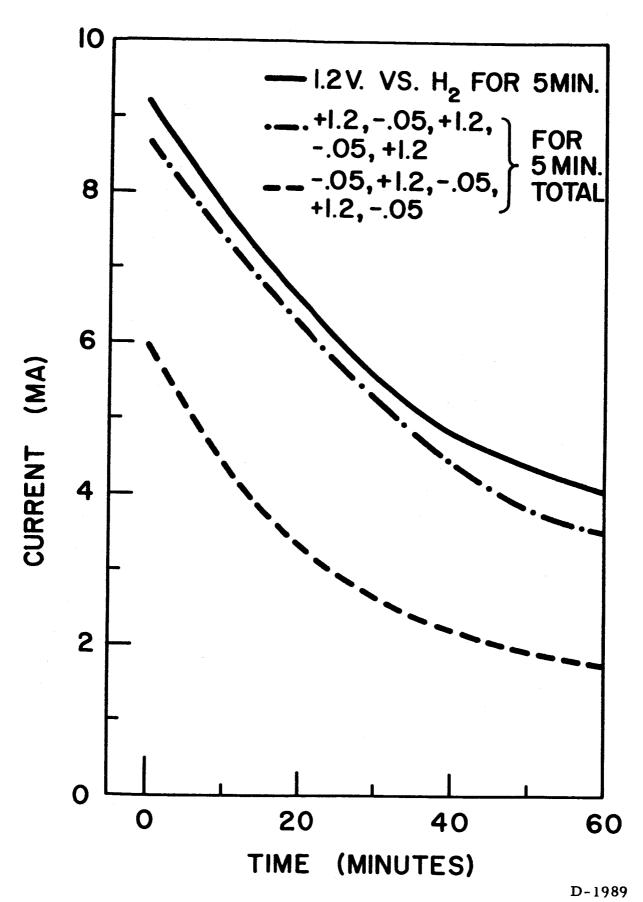
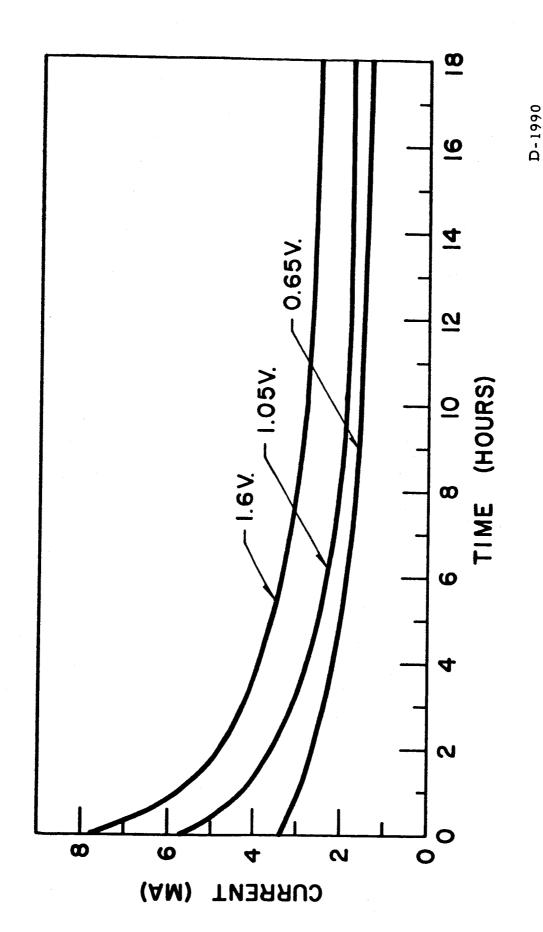


Fig. 6 Comparison of Pulse Cycling with Constant Potential for Activation of Pt-Pt Electrode.



Average Decay of Catalytic Activity of a Rh Anode in a H_2 -Saturated 1 N KOH Solution; Electrode Area = $20~\rm cm^2$. Fig. 7

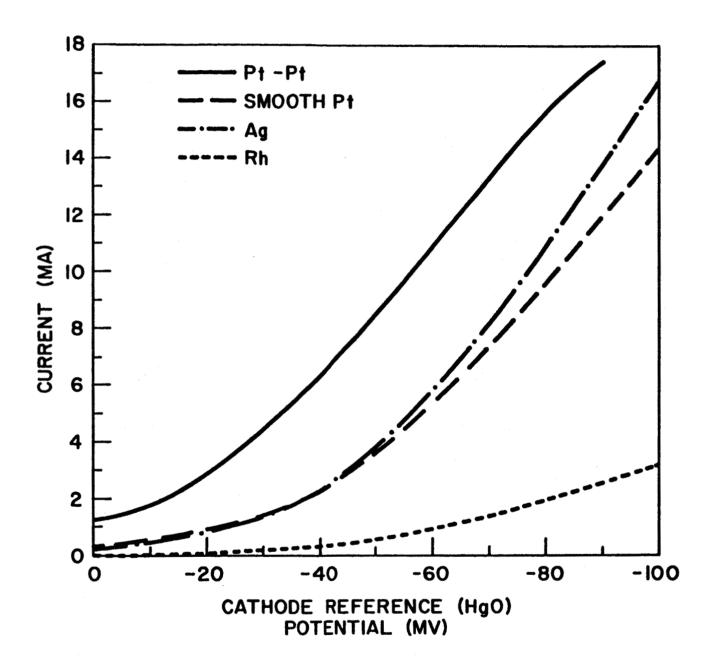


Fig. 8 Cathode Polarization Curves of Several Solid Metal Electrodes.

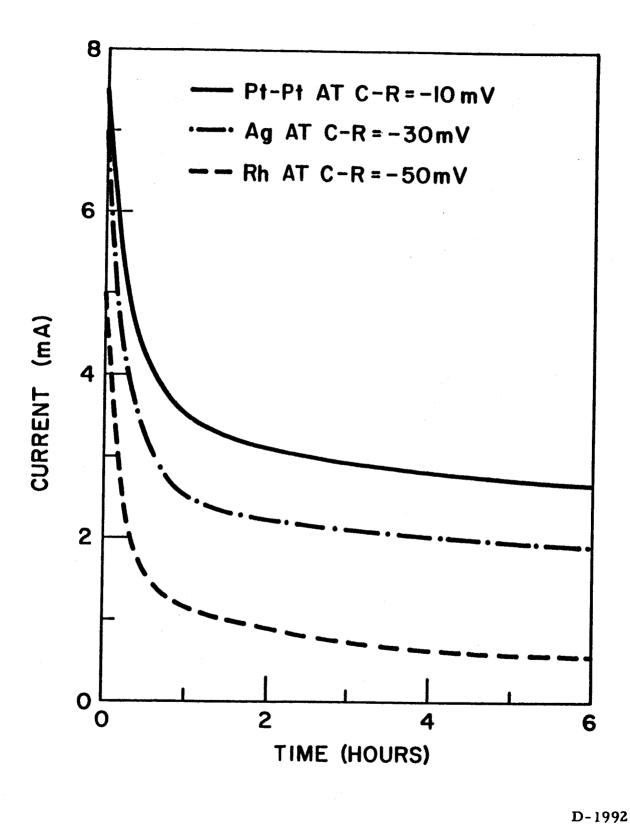


Fig. 9 Current-Time Curves for Discharge Pulsing of Solid Metal Cathodes at -0.700 mv; HgO Reference Electrodes.

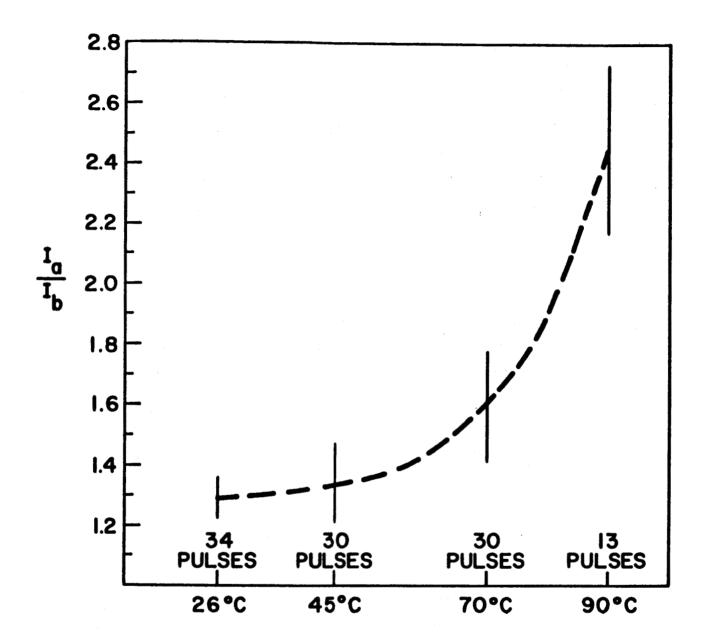
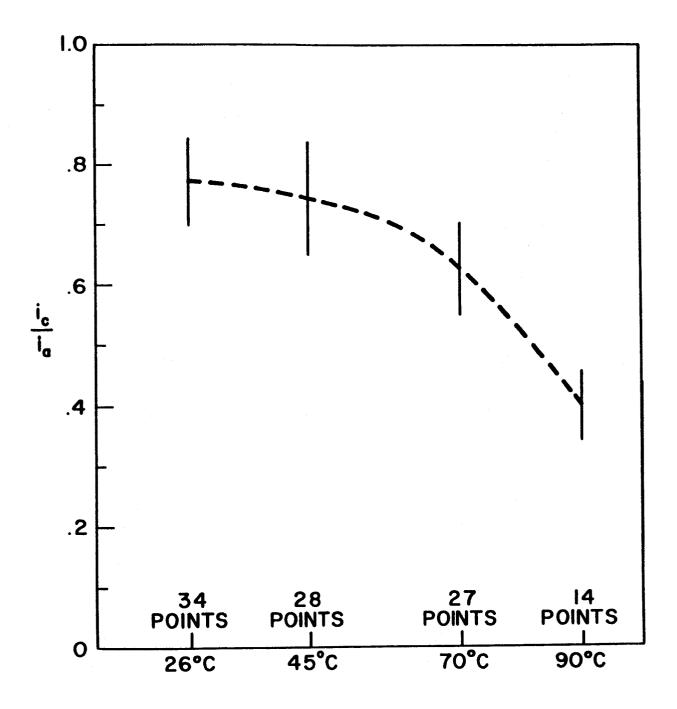
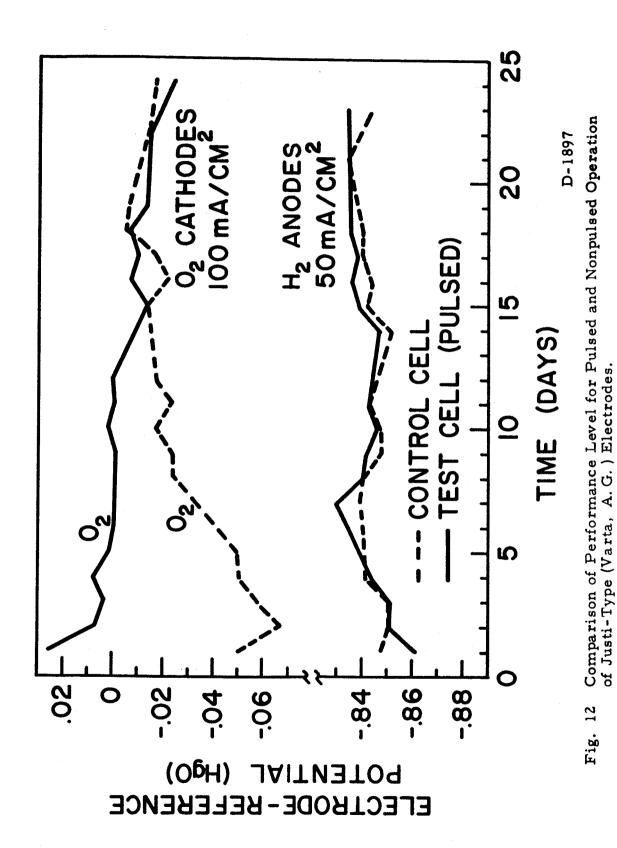


Fig. 10 Temperature Dependence of Improvement of Catalytic Activity Resulting from a Single Pulse; Smooth Pt in H_2 -Saturated 1 N KOH Solution; Pulse to $\eta = 1.6$ v for 30 Seconds.



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Fig. 11 Temperature Dependence of Decay of Catalytic Activity 30 Minutes after Activation Pulse; Smooth Pt in H_2 -Saturated 1 N KOH Solution; Pulse to η = 1.6 v for 30 Seconds.



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